

STUDY OF SOLAR CELLS WITH OPTIMIZED QUANTUM EFFICIENCY

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Abstract. *Substrate of silicon become classic, but costly in terms of technology and other strategic areas, was replaced by unconventional supports such as nanocomposites glasses, plastic materials Kapton type or metal foil of titanium and stainless steel. CIGS is the basic active element of the designed structure and represents magnetron target of CuInS₂ doped with Ga. The influence of Ga doping concentration is the main factor which may increase the quantum efficiency (Q_{eff}) of photovoltaic element, up to 17% - 19%, mean 5% more than the commercial products approved in the European market. Process, "Ion assisted RF magnetron sputtering" is the most reliable and versatile technique reported to MBE (molecular beam epitaxy).*

Keywords: solar cell, kapton, magnetron-sputtering

1. Introduction

The solar cell industry has grown quickly in recent years due to strong interest in renewable energy and the problem of global climate change. Currently, silicon solar cells rule the photovoltaic (PV) market. The best commercial Si PV modules have an efficiency of about 15-19% and cost between 4\$ and 5\$/Wp (Watts peak). PVs based on CdTe, CuInGaSe (CIGS), CuInSe (CIS), and organic materials are being developed with the aim of reducing the price per watt even if that means sacrificing conversion efficiency and reliability [1].

Silicon solar cells were initially used in the exploration of space, which remains an important application today [2]. Since their first development in the late 1950s, the efficiency of these cells has risen from 6% to more than 15%. This plus a decrease in cost and increase in production throughput has permitted companies to sell them for terrestrial use. In the 1980s, a new generation of solar cells based on III-V compound semiconductors, namely GaAs and InGaP, came into use in space applications [3]. Complex heterostructures based on arsenides and phosphide multijunction solar cells were developed and then realized on Ge substrates by means of metal-organic vapor phase epitaxy. Improvements in the 1990s

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permitted these solar cells to surpass the 20% efficiency mark, providing a significant boost to satellite power sources. Then, by the end of 2000, a triple junction InGaP/GaAs/Ge device had achieved 30% efficiency [4].

Recent research in the field of "electronics with thin films" focused specifically on the replacement of rigid glass substrates with metal sheet (titanium, stainless steel, molybdenum) or plastic (polyamide, polyvinyl fluoride, conductive polymers). The advantages of using substrates made of metal or plastic foils are those that, unlike glass, such solar cells are made thinner and lighter than conventional. Also such obtained devices are easy to use and can be used both in stationary applications and the mobile and portable applications (cars, space, mobile phones and even clothes).

Problems that may occur are mainly of technological nature but also the compatibility between substrates and semiconductor materials used as energy generators may cause some problems. In terms of technology, the first problem that can occur is that solar cells are subjected to mechanical work during the manufacturing process that can lead to damage of their curvature.

This has several consequences:

- change the device shape and size;
- due to differences in elastic modulus and chemical composition between layers, it can lead to cracking of default layers and less efficient solar cell.

2. Methods for obtaining photovoltaic cell

The use of technology radio frequency magnetron sputtering assisted ion beam is the best substitute for expensive technologies MBE (molecular beam epitaxy) [5], [6], [7]. The procedure for carrying out experimental model quantum efficiency solar cell with optimized results will bear all the technical constraints of the works executed on complex equipment, the class of radio frequency magnetron sputtering / VARIAN Elettrorava ER3119, assisted by a technological feature type Ion Gun / ANATECH LTD.

To achieve the alternating nanoscale photosensitive layers, technology can be explained by the following continuous flow, which requires a minimum of eight stages of processing on unconventional media (Kapton) of selected categories of new materials: titanium, stainless steel, molybdenum or polyamides, polyvinyl fluoride, conductive polymers.

Target active material $\text{CuInGa}^*\text{Se}_2/\text{S}_2$ (CIGS) is made in INFLPR laboratories and controlled thickness is deposited in very thin layer of Mo interface. Stringent control of dopant concentration of Ga (7-19)% is achieved by "making" the target and the successive measurements of complex equipment X-ray diffraction.

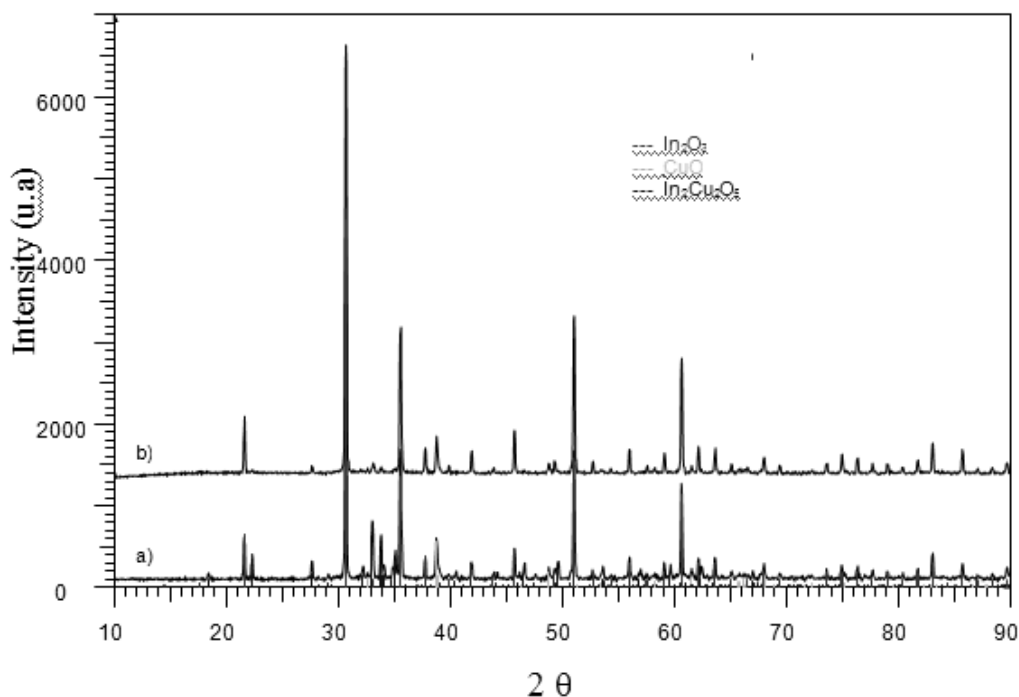


Fig. 1. a) X-ray diffraction pattern of the bulk sample.
b) X-ray diffraction pattern of the surface sample.

Samples were analyzed using D8 ADVANCE X-Ray Diffractometer (Bruker AXS) capable of qualitative analysis of polycrystalline materials, for both powder and bulk specimens.

The database is PDF-ICDD 2005, with over 170.000 files, covering all types of materials. In general we use Cu anode tube and for materials that contain cobalt and iron, we use the Mo anode, which is better suited.

Minimum step size: $2\theta = 0.0001^\circ$;

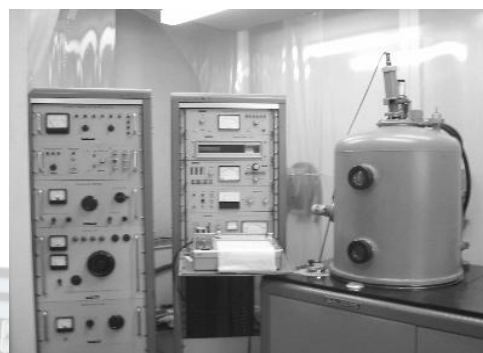
Maximum speed: $25^\circ/\text{s}$;

Acquisition range: $-110^\circ < 2\theta < 168^\circ$;

X-ray tubes with Cu and Mo anodes.

The samples were analyzed with the Cu tube, 0.04° step size and a speed of 2 seconds per step.

All materials: Mo, CIGS, ZnS, ZnO, Kapton and devices for adapting the magnetron target at the board cathode for "magnetron sputtering" are carefully processed (heating, vacuum degassing to evaporation temperature) in pre-deposition equipment Balzers BA510.

**Fig. 2.** BALZERS BA 510 Equipment.**Fig. 3.** VARIAN ER 3119 Equipment.

Materials are prepared in accordance with the characterization files from catalog as well as controlled parameters of the continuous flow developed technology.

Magnetron targets are mounted and processed in this specialized equipment VARIAN ER 3119. Coupling the magnetron cathode at motherboard can be made with optical contact at quite delicate standard industrial conditions, or using special devices – Mold of Cu HPFO/Cu of high purity and without oxygen [9].

**Fig. 4.** Mold of Cu.

3. Obtaining thin films for solar cells on kapton support

Obtaining of uniform films with optimal photovoltaic properties is subjected to the nature of material target (stoichiometry, degree of homogeneity, chemical stability) and the type of support and also the conditions of depositing. Preliminary experiments were conducted in laboratory for material synthesis and achieving targets for magnetron sputtering. To optimize the target composite nanostructures, research was done for the latest reports on obtaining materials CuInS_2 simple and doped.

Methods of preparation of materials are varied [1-9]:

1. Thermal synthesis method from precursors of type SSPs (single source precursors). This methods uses microwave radiation to increase the efficiency of materials preparation and to obtain a uniform material with reduced working time. Were obtained nanoparticles of chalcopyrite: CuInS_2 .

2. If the process starts from the alloy Cu /In, films are obtained by sulphating thin films of CuInS_2 deposited on glass coated with Mo.

3. Another method is to obtain films of CuInS_2 by pyrolysis process. CuInS_2 films were obtained by spraying aqueous solution ($\text{CuCl}_2 + \text{InCl}_3 + 3\text{SCN}_2\text{H}_4$) on vitreous substrate at temperatures from 250 to 420 ° C. CuInS_2 is formed as a product of solid phase reaction of binary sulfides of metals. CuS is formed at 250 °C by thermal decomposition of complex product $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl} \cdot 1/2\text{H}_2\text{O}$. Indium sulfide is formed by the reaction of indium chloride and indium thiocarbamide thermal decomposition.

4. By using alloy targets Cu-In introducing H_2S as working gas and the reaction atmosphere during the deposit by sputtering, films were obtained with S_2 on the glass substrate. Secondary phases Cu-In can coexist when the flow of H_2S is insufficient and excess gas can cause traces of elementary S in the films deposited.

5. CuInS_2 can be prepared by crystal growth from melt materials in the ternary system: - CuInS_2 - Sb_2S_3 - Bi_2S_3 .

6. Chemically we can obtain nanowires of CuInS_2 with diameter of 30-100 nm.

7. The advantage of using CuInS_2 to manufacture photovoltaic cells is the presence of nontoxic sulfur. CuInS_2 has the structure presented in figure 5.

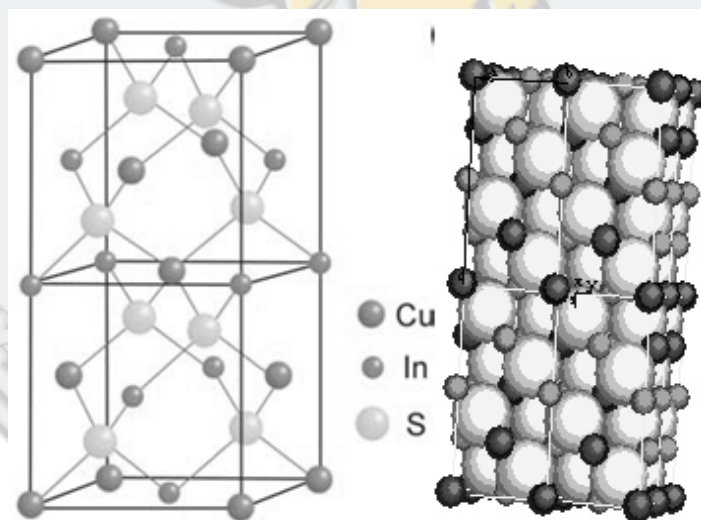


Fig. 5. Structure of CuInS_2 .

8. Optoelectronic properties of CuInS_2 are depending to chalcopyrite structure defects that can be crystallized in the CuAu structure called vacancies or ionic substitution.

9. Monocrystal of CuInS_2 (112) may be obtained by crystal growth from melt in argon atmosphere at pressure ~ 20 bar. Recent research on phase relations CuS - InS and Cu_2S - In_2S_3 indicates an incongruent melting for CuInS_2 [9].

10. By using the hydrothermal method in the presence of polyethyleneglycol (PEG). Were obtained CuInS_2 and CuInSe_2 with different morphologies, spheres, plates, bars and scales.

11. From liquid precursors, the advantage is the reduction of deposition and decomposition temperature to obtain films of CuInS_2 or $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$.

12. Obtain by sequential manufacturing of CuInS_2 in first stage involves the submission elements Cu and In on glass support first covered with Mo. Material deposited is heated to 500 °C with IR light and exposed to the atmosphere of sulfur vapor. Cu and In react with S_2 and form CuInS_2 .

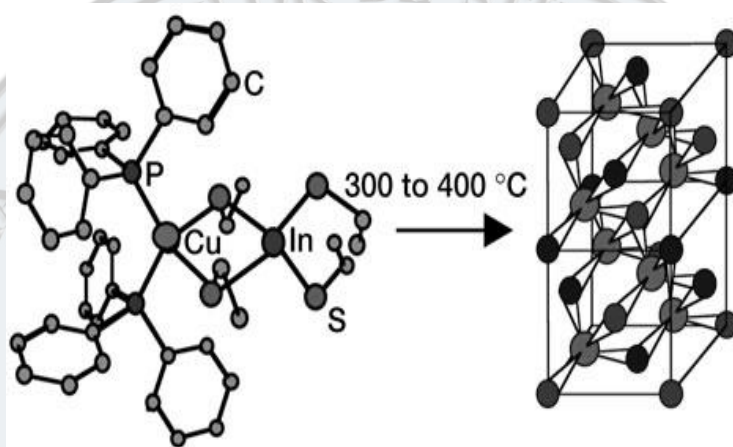


Fig. 6. Precursor decomposition to obtain the CuInS_2 .

13. Another method is to obtain CuInS_2 using three targets. In this case Cu, In and S_2 are taken simultaneously as a vapor on a heated substrate. This method is called co-evaporation. It also allows the use of rare earth doping. For making CuInS_2 , was used the experience of obtaining materials from the elements with binary compounds.

In the first case was proposed to be used Cu, In and S_2 . Dosing was made at analytical balance, mixing and heat treatment at temperatures 400 °C, 410 °C and 430 °C. They used aluminum crucibles. Samples were obtained in the form of discs of dimensions 20-30 mm diameter. Samples obtained were marked E_1 , E_2 and E_3 .

The second approach was the method starting from the sulphide of copper and indium. Were applied two types of preparation: ceramic method of making targets, which consists of preparing on the wet/dry way of a homogenous mixture, pressing mixture followed by heat treatment for sintering. It was used a hand hydraulic press Carl Zeiss Jena Germany with 400 kg/cm² maximum pressure. Oven bar superkanthal product type LHT 02/16 made by Nabertherm Germany with Maximum temperature of 1660 °C and controlled atmosphere of N_2 . The samples obtained were noted S_1 , S_2 and S_3 .

For obtaining solar cell deposition in continuous flow is done in a VARIAN ER3119 equipment which has two stations radio frequency magnetron sputtering and one ion gun with energies up to 1500 eV.

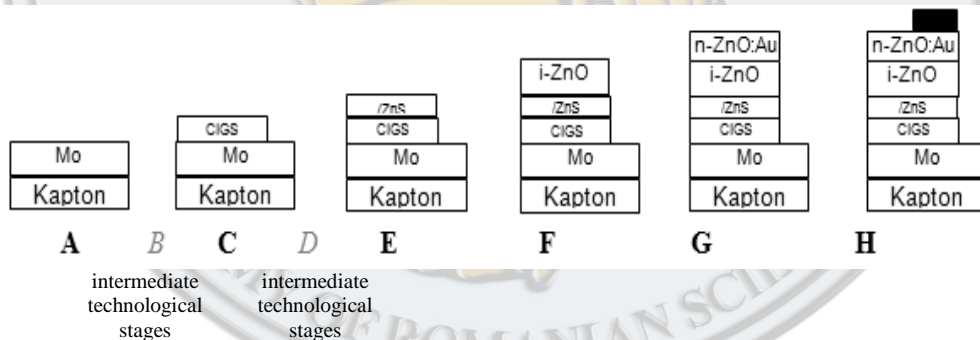
The device is equipped with a cryogenic pump with the working pressure limit of 2×10^{-7} Torr and with a system to control layer thickness during deposition of the quartz balance type, MAXTECH type, INC. - Model TM 200R.

Deposition rate is optimized for each type of material to eliminate the mechanical stress and the occurrence of inclusions or spraying the material on the active surface of the designed photovoltaic element. As support material of the photovoltaic element, was elected Kapton, a flexible material, light and with an optical structure close to a performing optical regular used component.

Technological process parameters: working pressure, substrate temperature during depositing, the flow volume of the gas of assistance, the evaporation rate and the operating status of radio frequency sources and balance active power/reactive power are controlled in place.

The quality of the materials (surface morphology, crystalline phase formation and structures compositional uniformity in the depth of nanoscale layers) from which magnetron targets are prepared, is a basic element for making thin films of good optical quality and reproducible compared with the selected substrate and temperature range during the process flow under control.

Flow diagram for obtaining of the experimental solar cell model is the following:



A = Mo deposit, **B** = mask, **C** = deposit Cu/In / Ga / Se / S, **D** = 500 °C treatment, **E** = chemical filing with ZnS, **F** = tracing – depositing i-ZnO, **G** = depositing n-ZnO:Al/Au; **H** = tracing electrodes.

Observations

- It is very important in order to preserve energy compatibility of designed thin layers interfacing of Kapton support with a nanometric film of Si. Commercial thicknesses are between 50 nm and 100 nm.

- In experiments we have opted for thin layers, in terms of obtaining optimum energy efficiency, as for Si we deposited by the proposed method (50 ± 5) nm.

- Our experiments have emphasized the importance of the Mo buffer layer, that the interface at CuInGaS_2 is in danger of creating a parasite interlayer of MoS_2 at increase of the substrate temperature.

The formation of this parasite interlayer of MoS_2 drastically affects electronic properties of the photovoltaic device/solar cell. This is another technical reason that we chose Kapton as substrate with a stable thermal reaction. It was made the deposit in the proposed process flow sequence for the experimental model of solar cell as follows: Mo layer thickness of 700 nm was deposited with the sputtering rate ($0.7 \div 1$) Å/sec; active CIGS layer maximum thickness of 1500 nm was made with a sputtering rate of 1.5 Å/sec; photoactive ZnS was deposit with a sputtering rate of ($6.5 \div 7$) Å/sec. at total thickness of 50 Å; i-ZnO at maximum thickness of 500 nm and n-ZnO: at thickness of 800 nm were made with a sputtering rate of ($0.5 \div 1$) Å/sec. Deposition of modular elements of the experimental model of solar cell was made on Kapton support by radio frequency magnetron sputtering technology- ion beam assisted in inert gas –argon- of 99.99% purity. Developing of experimental demonstrative and functional model aims to achieve an optimized quantum efficiency and conversion efficiency in the range $14\% \div 20\%$ [5].

4. Conclusions

(1) Target active material $\text{CuInGa-Se}_2/\text{S}_2$ (CIGS) is produced in INFLPR laboratories and is deposited in controlled thickness in very thin layer of Mo interface. Stringent control of dopant concentration of Ga ($7 \div 19\%$) is achieved after "making" the target, with successive measurements on X-ray diffraction complex equipment. In figure 7 is presented sample diffractometry with identifying the diffraction lines.

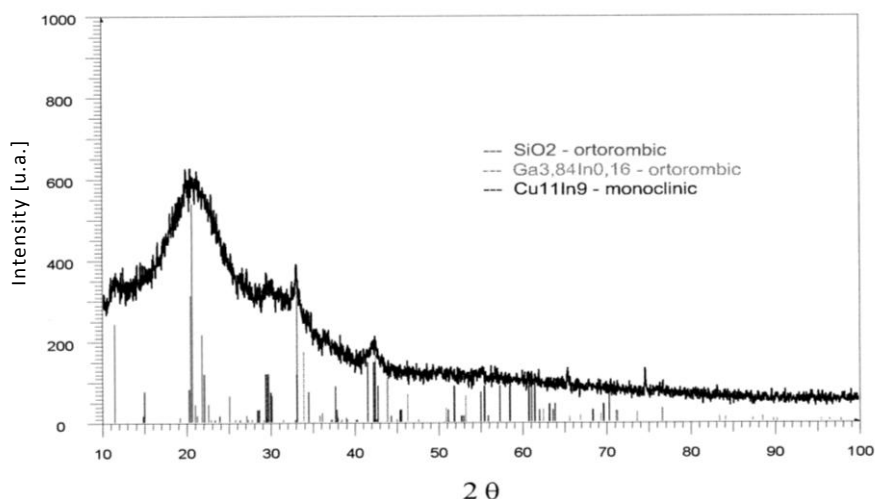


Fig. 7. Spectrum of the sample composite target CuInGaS_2 for the experimental model.

Phasal composition of samples analyzed is:

SiO_2 - majority phase, amorphous;

$\text{Ga}_{3,84}\text{In}_{0,16}$ - minority phase, crystallized in the system orthorhombic;

$\text{Cu}_{11}\text{In}_9$ - minority phase, crystallized in the monoclinic system.

Specific thickness of layers of Mo, CIGS, ZnS, ZnO, Au is measured in situ and the control range is between 20 nm and up to 2000 nm.

(2) No occurrence of sulfur in crystalline structures, but a large part of the sample is in amorphous form.

(3) Reporting the peak areas corresponding sites in total area phases arise as a phase of $\text{Ga}_{3,84}\text{In}_{0,16}$ percent occur in approximately 2.6% in the sample, resulting that the percentage of Ga (found in a crystalline structure) of the sample is 2.5% [9].

(4) It is known, taking into account the latest information technology in the field of literature, the procedure of radio frequency magnetron sputtering, ion beam assisted average energy, it must be commercially viable as a variant [8].

The process completed and adopted as technology at this stage of decision is pure and clean.

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